Fundamentals and Applications of Dielectric Ceramics
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Lecture No 10
Concentration and effect of intrinsic impurities

So, welcome again to the new lecture of the course, Fundamentals and Applications of Dielectric Ceramics. So, we will just briefly recap what we did in the previous lecture.

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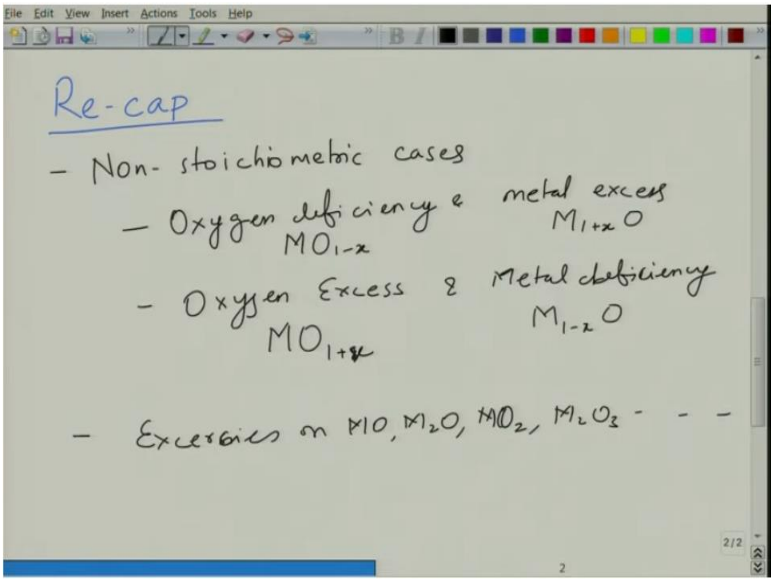

Re-cap

- Non-stoichiometric cases
  - Oxygen deficiency & metal excess
    MO_{1-x} $M_{1+x}O$
  - Oxygen Excess & Metal deficiency
    MO_{1+x} $M_{1-x}O$
- Excersies on MO, M_2O, MO_2, M_2O_3 - - -

In the previous lecture, we looked at non-stoichiometric oxides primarily. So, we looked at two dominant cases of oxygen deficiency and metal excess or we looked at oxygen excess and metal deficiency, right. So, the first one can be determined as MO_{1-x}, this could be $M_{1+x}O$, this could be MO_{1+x} and this could be $M_{1-x}O$, okay. So, essentially in the first case you form vacancies of oxygen and they can be compensated either electronically by forming electrons or they can be formed by reduction of metal at metal sites.

In case of metal excess, you form metal interstitials, which can be again compensated by formation of electrons or reduction of metal site. Generally, you do not talk about changes in the cation valances. So, generally it is metal which reduces and oxidizes. And oxygen excess can be accommodated by formation of oxygen interstitials, which can be compensated by formation of either holes or metal oxidation, okay.

And metal deficiency can be accommodated by formation of metal vacancies, which are compensated by formation of holes or again oxidation of metal ions and there are various oxides which follow these things. And as a homework, I requested you to do exercises on MO, M_2O, MO_2, M_2O_3 and so on and so forth. So, this will allow you to understand and just ensure that you have site balance, you are mass balance and you have charge balance. You have to preserve these three to right correct defect reactions.

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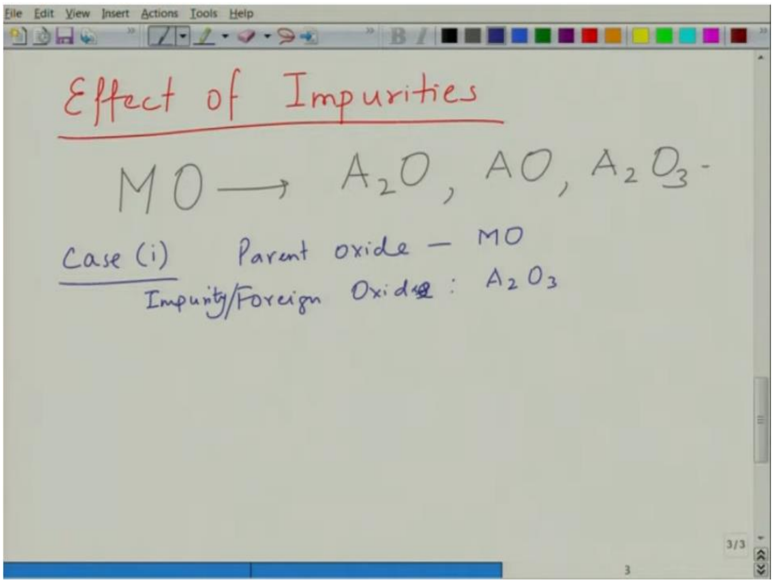

Effect of Impurities

$MO \longrightarrow A_2O, AO, A_2O_3$ -

Case (i) Parent oxide — MO

Impurity/Foreign Oxide : A_2O_3

Now, let us look at another case, which happens in oxides, which contributes to defect chemistry in a very significant way, that is effect of impurities and the reason for that is because nothing is pure in nature, okay. Thermodynamics itself prefers the impurities and as a result, there are always impurities present. So, if you have oxide MO, you might have impurity which is $M_2'O$, M' is probably not a good idea, let us say I have impurity which is A_2O.

I can have impurity, which is AO, I can have impurity which is A_2O_3 in very small amounts and these impurities could be either substitutional or they could be interstitial, okay. Depending upon how they are present, what kind of valences of these cations are affect the defect chemistry of the parent material. So, let us say the case one, in which the parent oxide is MO and foreign oxide is or you can say impurity oxide is A_2O_3, okay.

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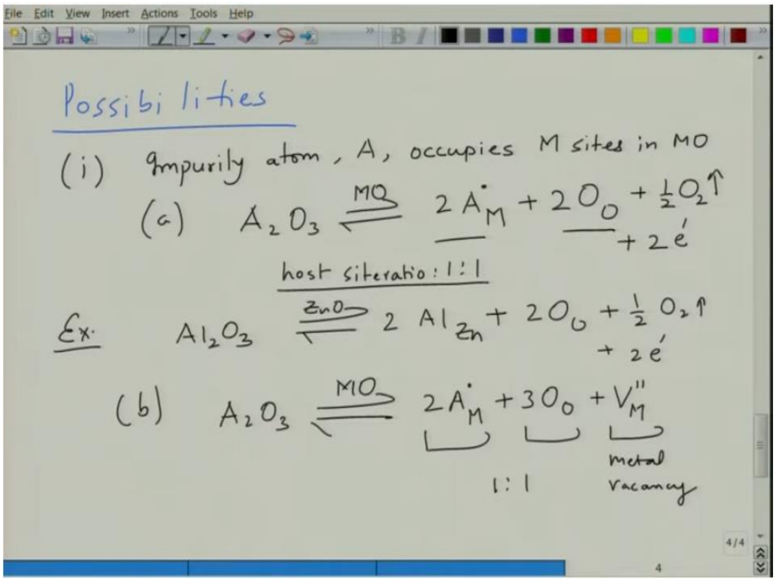

Possibilities

(i) Impurity atom, A, occupies M sites in MO

(a) $A_2O_3 \underset{}{\overset{MO}{\rightleftharpoons}} \underline{2A_M^{\bullet}} + \underline{2O_O} + \frac{1}{2}O_2\uparrow + 2e'$

host site ratio : 1:1

Ex. $Al_2O_3 \overset{ZnO}{\rightleftharpoons} 2Al_{Zn} + 2O_O + \frac{1}{2}O_2\uparrow + 2e'$

(b) $A_2O_3 \overset{MO}{\rightleftharpoons} \underbrace{2A_M^{\bullet}} + \underbrace{3O_O}_{1:1} + \underbrace{V_M''}_{\text{metal vacancy}}$

So, what are the possible scenarios? You can have various possible scenarios. So, the first possibility is that this impurity atom, which is A occupies M sites in MO, okay.

$$A_2O_3 \overset{MO}{\leftrightarrow} 2A_M^{\bullet} + 2O_O + {}^{1}\!/_{2}\, O_2 \uparrow + 2e'$$

Now, if that happens, let us say A2O3 goes to MO, okay. So, which means 2A go to M site, okay. What must happen? MO host lattice has a site ratio of 1:1, right, this is the host site ratio and impurities cannot disturb that. So, when two A go to M site, two oxygens go to oxygen site. So, site ratio is maintained, which means the oxygen has to go out. Now, this A is 3+ M is 2+, which means it will carry one positive charge. How is this going to be accommodated, by creation of electron. So, this is going to give rise to two electrons. So, this is electronic compensation, which means impurity A2O3 type will cause a n- type behavior in.

So, just like example could be if you have Al2O3 which let us say goes into ZnO. What will happen?

$$Al_2O_3 \overset{ZnO}{\longleftrightarrow} 2Al_{Zn}^{\bullet} + 2O_O + {}^{1}\!/_{2}\, O_2 \uparrow + 2e'$$

This is 2Al going to zinc site. So, this is example, plus two oxygen going to oxygen sites and another oxygen goes out and then two electrons. So, basically doping of aluminum into zinc oxide has created electrons. So aluminum doped zinc oxide is n-type semiconductor and that is what it is. The aluminum doping of zinc oxide makes it a n-type conductor. This is something that you do purposefully, but if you do not do purposefully, this might happen inadvertently, if you have impurities present. What is the other possibility?

So, this is the first possibility. What is the other possibility? The other possibility is A2O3 is in MO, 2AM plus let us say all the three oxygens go to oxygen site.

$$A_2O_3 \overset{MO}{\leftrightarrow} 2A_M^{\bullet} + 3O_O + V_M''$$

Now, the site balance is disturbed because you have created three oxygen sites, but you have only two metal sites, which means one of the metal sites will be vacant. So, this is ionic compensation, you will create metal vacancy. So, this is electronic compensation, this is ionic composition. Again, the charge balance, the mass balance, the site balance has to be maintained.

Site balanced by creating a metal vacancy is 1:1, if you did not have that, then you will have site imbalance. In the previous case, only two oxygens went to oxygen sites, one of the oxygen went out, so again the site balance was maintained. And site balance is that of the host lattice not of the foreign lattice, okay, is that of the host lattice because the host lattice is the one which is accommodating the impurity, not the other way round. If you have other way round, you will have to do it other way round, okay. So, this is one possibility.

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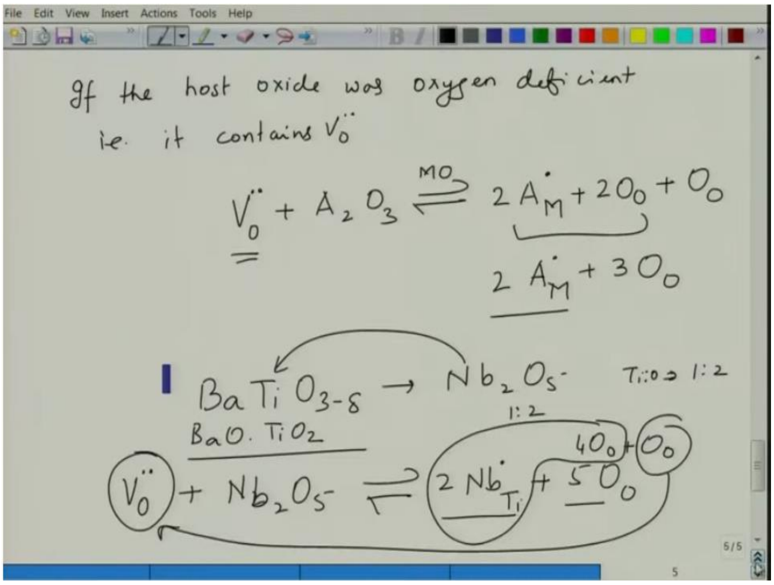

If the host oxide was oxygen deficient
i.e. it contains $V_O^{\bullet\bullet}$

$$\underline{\underline{V_O^{\bullet\bullet}}} + A_2O_3 \overset{MO}{\rightleftharpoons} \underbrace{2A_M^{\bullet} + 2O_O} + O_O$$

$$\underline{2A_M^{\bullet}} + 3O_O$$

$$BaTiO_{3-\delta} \rightarrow Nb_2O_5 \qquad Ti:O \Rightarrow 1:2$$

1:2

$$\underline{BaO.TiO_2}$$

$$V_O^{\bullet\bullet} + Nb_2O_5 \rightleftharpoons \underline{2Nb_{Ti}^{\bullet}} + \underline{5}O_O$$

$$4O_O + O_O$$

Now, another thing which this impurities are used for is, imagine if the host oxide was, so you can use it positively, let us say, if the host oxide was oxygen deficient, that is, it contains VO, to begin with. So, you want now get rid of oxygen vacancies, what do you do then. You have oxygen vacancies to present in the system, which means, if I am doping with an oxide with higher valence, which means I am bringing in extra oxygen to the system.

So, if I am bringing in A2O3 and this goes to MO, then basically two A go to M site, two O go to oxygen site, to maintain the site stoichiometry, but you have one oxygen vacant site. This oxygen vacant sites can be filled by this again oxygen site. So now you do not disturb the site balance, you had one site here, you have filled that site with extra oxygen and two other sites which were created, they are balancing each other.

So, this is basically another ways we can write this as, this is positively charged, this is again positively charged, so you have positive charges balancing each other, the sites balancing each other and the, so essentially you can write this as

$$V_O^{\bullet\bullet} + A_2O_3 \overset{MO}{\leftrightarrow} 2A_M^{\bullet} + 3O_O$$

Site balance is there, because you have two metal sites and one of the oxygen sites is compensated by this site and for the two metal sites, you have two metal sites, okay. So, site balance, mass balance and charge balance is there, alright.

So, this is how, you can use it to your advantage. If you want to reduce the oxygen vacancy concentration in oxide, you can dope it with the oxide with higher valence, okay. So, you can dope, one example could be, let us say, we have $BaTiO_{3-\delta}$, it has oxygen vacancies. So, if I dope it with, let us say Nb_2O_5, niobium goes to titanium site, okay. So, basically what is it? It is $BaO.TiO_2$, barium titanate, right.

So, if you put niobium in this, Nb_2O_5, you have vacancies of oxygen in the system. So, two niobium go to titanium site plus five oxygens go to oxygen site. So, this niobium will be positively charged. So, out of these four are related to titanium, so because Ti:O is 1:2, right. Okay, so out of these five, so you can write this $4O_O + O_O$, so this is site balance 1:2 and this is compensated by this extra one.

$$V_O^{\bullet\bullet} + Nb_2O_5 \leftrightarrow 2Nb_{Ti}^{\bullet} + 5O_O$$

So, this is how barium titanate is made more resistant, okay.

So, barium titanate may have electronic defects, it has oxygen vacancies. So, how do you eliminate oxygen vacancies? You bring in extra oxygen into the system by doping it with the oxide of higher valence. This is called as compositional engineering of oxides. So, not only impurities can give you defects, but impurities can also be used to compensate the defects which exists from earlier, okay.

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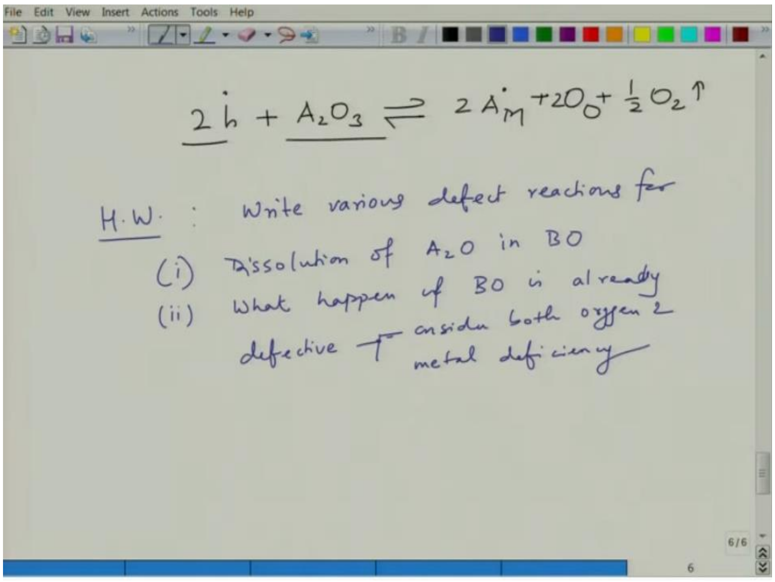

$$\underline{2\dot{h}} + \underline{A_2O_3} \rightleftharpoons 2A_M^{\cdot} + 2O_O + \frac{1}{2}O_2\uparrow$$

H.W. : Write various defect reactions for
(i) Dissolution of A_2O in BO
(ii) What happen if BO is already defective → consider both oxygen & metal deficiency

Alternatively, if you have let us say holes in the system, in this case if you had holes in the system, if the system had holes, then you again dope it with A2O3, then 2A go to M site + 2O go to O site and this becomes half O2.

$$2h^\bullet + A_2O_3 \leftrightarrow 2A_M^\bullet + 2O_O + {}^1/_2\, O_2 \uparrow$$

So, you can reduce the whole concentration by doping it with a higher valence oxide. So, basically you can reduce the amount of defects if your oxide was already defected, okay. So, appropriately you can choose, for MO, you will choose M2O3, but for M2O, you can choose MO, okay.

Alternatively, if you wanted to control the metal vacancies, then you will have to go for lower valence stuff. So, that is how you do so, what I would like you to do is that as a homework you should do, write various defect reactions for dissolution of A_2O and BO, okay, do the other way around and then what happens if BO is already defective. Consider both oxygen and metal deficiency, okay. So, do this as a homework, this will be useful for you to understand the cases that we have done just now, alright.

Now, the next thing is to look at, so, what we have looked at until now is we have looked at the stoichiometric defects, which do not change the stoichiometry of the oxide, like Frenkel defects, Schottky defects, and then we looked at the cases of non-stoichiometric oxides where you have oxygen vacancy, you have oxygen excess or metal excess or oxygen deficiency or metal deficiency. And depending upon ionic or electronic compensation, you will form appropriate defects.

The most important thing to consider is site balance, mass balance and charge balance. If you get it right, you will get the defect reactions right. If you do not get it right, then you will not get the defect reactions right. But they are very simple to understand, you just have to match the, there should be no extra sites in the system, there should be no extra masses in the system, there should be no extra charges. Solid eventually has to be charged neutral whatever you do, okay.

Now, let us say, so some of these materials also contain. Now, we know from elementary thermodynamics that things like vacancies and metals they are defects which exist under equilibrium, okay. So, similarly, in these oxides, these defects depending upon the energy of these defects, the defects formation energy, whether Schottky defects or Frenkel defects or anti-Frenkel defects, these defects will exist thermodynamically. So, we would like to calculate the concentration of intrinsic defects in a given system.

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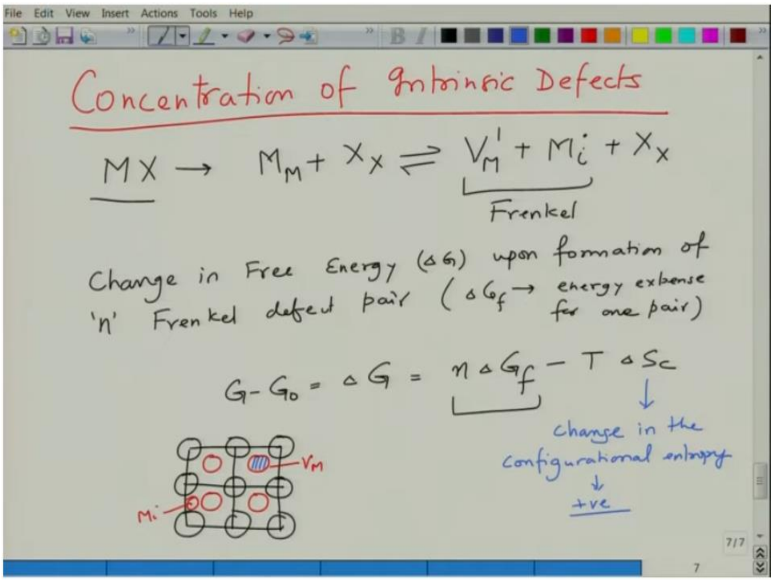

Concentration of Intrinsic Defects

$$\underline{MX} \rightarrow M_M + X_X \rightleftharpoons \underbrace{V_M' + M_i^{\cdot}}_{\text{Frenkel}} + X_X$$

Change in Free Energy (ΔG) upon formation of 'n' Frenkel defect pair ($\Delta G_f \rightarrow$ energy expense for one pair)

$$G - G_0 = \Delta G = \underbrace{n \Delta G_f} - T \Delta S_c$$

$\Delta S_c \downarrow$ change in the configurational entropy $\downarrow$ $\underline{+ve}$

So, let us say we consider Frenkel defect. So, let us say we consider a halide MX and in that the reaction can be written as

$$M_M + X_X \leftrightarrow V_M' + M_i + X_X$$

and x remains at x site, so this is a Frenkel defect, they do not change the stoichiometry, stoichiometry remains same, the site balance same, there is one metal site, there is one anion site and interstitial site is a site anyway, it is a interstitial site, so we do not create any extra sites in the system.

So, what you are creating is a pair of metal interstitial and metal vacancy. So, free energy change, change in free energy, that is delta G upon formation of, let us say, n number of Frenkel defect pairs, because they have to form in the pair. So, let us say we form n pair and what is the delta G that happens and we say that ΔG_f is the energy of expense for one pair, okay. So,

$$G - G_0 = \Delta G = n\Delta G_f - T\Delta S_C$$

So, this is the change in enthalpy, which is nothing but number of defect pairs multiplied by the energy that you need to create one pair, okay, that is ΔG_f, you can write it as ΔH_f if you want. But, the moment you create these defects, there will also be a change in the entropy and most importantly the configurational entropy because earlier you were starting a system like this. So, you had a system, which was like this, then a perfect material system would be like this, right.

Now, imperfect would be, you create this as a vacant site and this will go somewhere, let us say here, the interstitial site. So, this will be M_i, this will be V_M, but now, where can you put it, the configuration has changed, it does not need to be here, it can be somewhere else. So, there are various possible configurations, as a result your configuration entropy will change. So, ΔS_C is nothing but change in the, basically it represents the number of ways in which you can arrange these species, entropy and this is actually positive in nature, okay.

So, basically the equilibrium concentration of defects this n will be, so there will be certain finite value of n only if the free energy is negative at that point. There has to be free energy minimization, which means we would like to minimize this free energy with respect to n, okay, to find out the value of n at which free energy is minimum.

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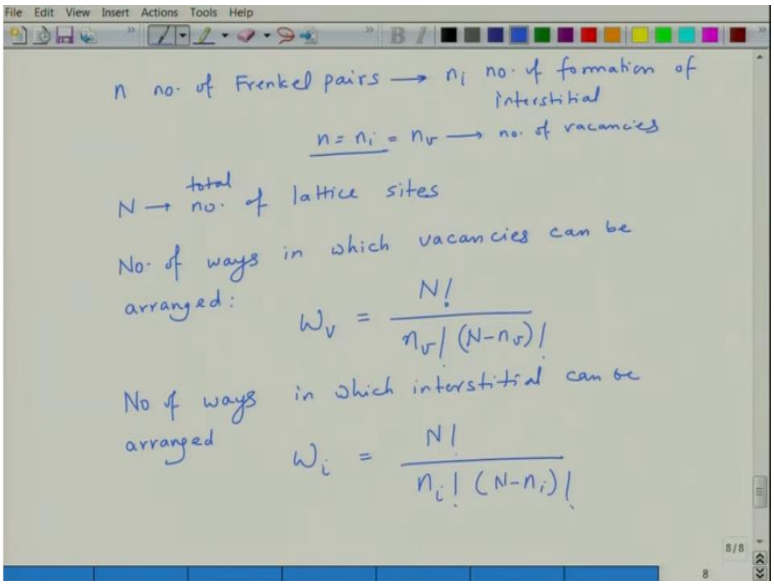

n no. of Frenkel pairs → n_i no. of formation of interstitial

$\underline{n = n_i} = n_v$ → no. of vacancies

N → total no. of lattice sites

No. of ways in which vacancies can be arranged:

$$W_v = \frac{N!}{n_v!\,(N-n_v)!}$$

No of ways in which interstitial can be arranged

$$W_i = \frac{N!}{n_i!\,(N-n_i)!}$$

So, we need to do certain things. So, let us say, you have number of Frenkel pairs is n, so n number of Frenkel pairs, they lead to basically ni number of formation of interstitials, right. And n is nothing but

$$n = n_i$$

okay, n number of pairs and each pair will contain one interstitial and one vacancy. And similarly, it will also be equal to n_v, which is number of vacancies, right. So, we write this

$$n = n_i = n_v$$

assuming that N is the total number of lattice sites, okay.

So, number of ways to arrange the vacancy is, we can write let us say, this is equal to Wv, so

$$W_V = \frac{N!}{n_v!\,(N - n_v)!}$$

Similarly, the number of ways in which interstitials can be arranged, that is

$$W_i = \frac{N!}{n_i!\,(N - n_i)!}$$

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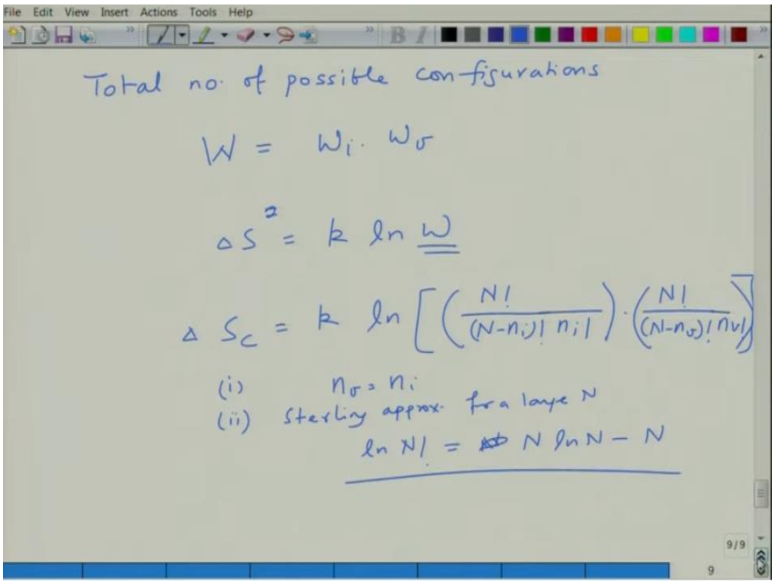

Total no. of possible configurations

$$W = W_i \cdot W_v$$

$$\Delta S^{2} = k \ln \underline{\underline{W}}$$

$$\Delta S_c = k \ln \left[\left(\frac{N!}{(N-n_i)!\,n_i!} \right) \cdot \left(\frac{N!}{(N-n_v)!\,n_v!} \right) \right]$$

(i) $n_v = n_i$

(ii) Sterling approx. for a large N

$$\ln N! = N \ln N - N$$

So total number of possibilities is

$$W = W_i \cdot W_v$$

, alright. So, you just basically multiply this and you can do the math by yourself by applying Stirling approximation and so on and so forth. So, if you do the and

$$\Delta S = k ln W$$

, right and you replace this W in this form, what you will get is essentially

$$\Delta S_C = k\ ln \left[\frac{N!}{(N - n_i)!\,n_i!} \frac{N!}{(N - n_v)!\,n_v!} \right]$$

And since we know that $n_v = n_i$ and we apply.

So first condition is $n_v = n_i$, second approximation is Stirling approximation, for a large N that is $\ln N! = NlnN - N$, okay, for large numbers we make this approximation.

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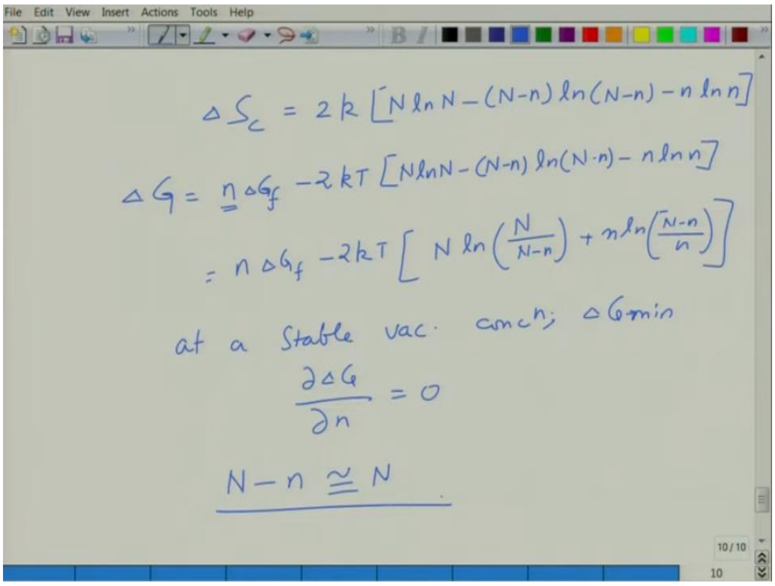

$$\Delta S_c = 2k\left[N\ln N - (N-n)\ln(N-n) - n\ln n\right]$$

$$\Delta G = \underline{\underline{n}}\,\Delta G_f - 2kT\left[N\ln N - (N-n)\ln(N-n) - n\ln n\right]$$

$$= n\,\Delta G_f - 2kT\left[N\ln\left(\frac{N}{N-n}\right) + n\ln\left(\frac{N-n}{n}\right)\right]$$

at a Stable vac. conc^n; ΔG min

$$\frac{\partial \Delta G}{\partial n} = 0$$

$$\underline{N - n \cong N}$$

If you apply this, then what we get is, so you can do the math yourself, we need to

$$\Delta S_C = 2k[NlnN - (N-n)\ln(N-n) - nlnn]$$

And hence the total energy change is

$$\Delta G = n\Delta G_f - 2kT[NlnN - (N-n)\ln(N-n) - nln\,n]$$

, okay. And so, we can write this as let us say, we write this as, and just do some more changes here so just do some more approximations, you will get something like that, okay, you will get these expressions.

$$\Delta G = n\Delta G_f - 2kT[Nln\left(\frac{N}{N-n}\right) + nln\left(\frac{N-n}{n}\right)]$$

Now, what you have to do is that if vacancies were stable defects, then at certain concentration, the free energy would be minimum, that means, at stable vacancy concentration or defect concentration, ΔG should be minimum, so which mean

$$\frac{\partial \Delta G}{\partial n} = 0$$

, okay. We must get some solution at that point and we also assume N – n is almost equal to N because n and is very small as compared to its, the order of PPM or even lower.

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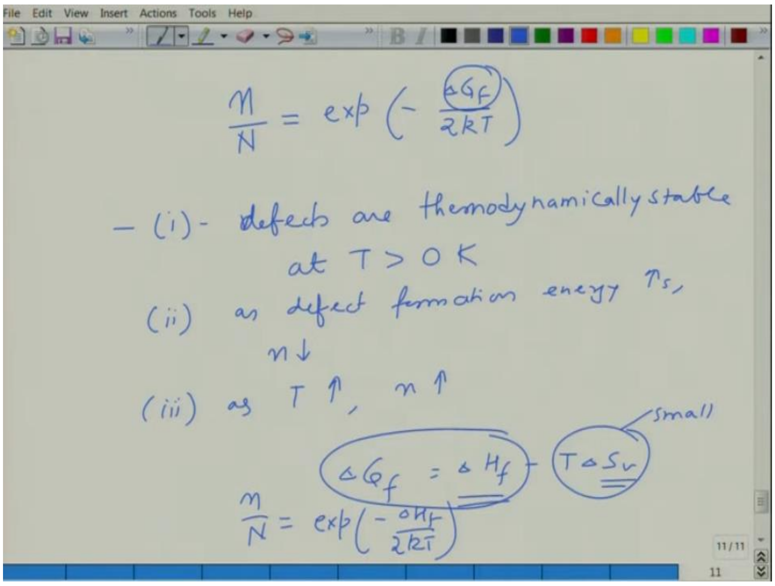

$$\frac{n}{N} = \exp\left(-\frac{\Delta G_f}{2kT}\right)$$

- (i) - defects are thermodynamically stable at $T > 0\ K$
(ii) as defect formation energy ↑s, $n \downarrow$
(iii) as $T \uparrow$, $n \uparrow$

$$\Delta G_f = \Delta H_f - \underbrace{T \Delta S_v}_{\text{small}}$$

$$\frac{n}{N} = \exp\left(-\frac{\Delta H_f}{2kT}\right)$$

So, if we make that approximation, then we can work out this as

$$\frac{n}{N} = exp\left(-\frac{\Delta G_f}{2kT}\right)$$

So, this is what basically it works out to, that there is a equilibrium vacancy concentration, which is proportional to ΔG_f, exp-ΔG_f. So, basically what it says is that, one, defects are thermodynamically stable at t greater than 0 kelvin, so as long as temperatures are more than 0 kelvin, they are stable, okay.

Two, as defect formation energy goes up, energy increases, n will decrease, which means, the more the energy required from the defects, the lower the number, which makes sense and third is as temperature increases, n increases and this happens in an exponential manner. You can further simplify this, you can write this

$$\Delta G_f = \Delta H_f - T\Delta S_v$$

where ΔH_f is enthalpy of formation of defects and ΔS_v is nothing but vibrational entropy change.

But it is approximated as ΔG_f to be equal to ΔH_f because the vibrational entropy change is very small. So, this is very small and hence you approximate this as

$$\frac{n}{N} = \exp\left(-\frac{\Delta H_f}{2kT}\right)$$

, where H_f is basically the enthalpy of formation of defects, okay. Similarly, for Schottky defects, you can write this similar expression you will, so this is 2kT, sorry not 1kT, 2kT. In metals you have 1kT and in stoichiometry oxides you have 2kT, okay.

Similarly, you can get for Schottky defects also, which I am sure you can work out easily. So we will stop here. What we have done is basically we have looked at the cases where you can form defects upon dissolving impurity or you can put impurity to change its characteristics and we have also seen how Schottky and Frenkel defects are stable defects thermodynamically, and we can calculate their concentration in a simple manner. So, we will stop here, we will further proceed on this in the next class. Thank you.